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The Underpotential Deposition of Copper on Pt(311): Site Selective Deposition and Anion Effects

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The Underpotential Deposition of Copper on Pt(311): Site Selective Deposition and Anion Effects

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ABSTRACT

The underpotential deposition of copper on Pt(311)=Pt[2(111)x(100)] stepped surfaces has been studied and the results are compared with those for the same processes on Pt(111) and Pt(100). We find that the adsorption/desorption of copper on the (111) (terrace) and (100) (steps) sites of this surface takes place at different potentials so that selective adsorption on terrace or step sites is possible. The potentials, and their relative position, are different from those on Pt(111) and Pt(100) surfaces. These differences are ascribed to competitive effects from the anions which adsorb more strongly on the (100) than on the (111) sites. In addition, the presence of halides (Cl^-, Br^-) dramatically affects the electrodeposition process.

INTRODUCTION

There have been numerous studies devoted to the phenomenon of underpotential deposition (UPD) of copper on platinum basal single crystal electrodes, especially on Pt(111) [1-16]. In these studies much emphasis has been placed on the effects of halides as well as other adsorbates on the deposition and stripping processes. However, there is a lack of information regarding this same surface process on platinum stepped surfaces. Scortichini and Reilley studied the upd of Cu on Pt(331) [17] and Pt(311) [17,18] along with platinum basal single crystal electrodes. However, the pretreatment of the electrodes was not the most appropriate, especially in the case of Pt(311), so that surfaces with a large number of defects resulted. As a consequence of this lack of order, the corresponding voltammetric profiles were rather featureless. This precluded any quantitative or semiquantitative interpretation of the data. In spite of this, these studies are interesting from both fundamental and technical points of view.

The use of stepped surfaces of varying terrace width may have profound effects on electrodeposition since it will affect the step-site density. Step-sites are known to act as very active sites in metal adatom deposition and studying how the deposition varies as a function of the step-density may provide a wealth of information. For example it would be most interesting to determine if there is a threshold value in the step-site density where significant changes are evident.

In this paper, we present experiments on the underpotential deposition of copper on a Pt(311)=Pt[2(111)x(100)] electrode surface. This is a stepped surface with (100) steps and (111) terraces and with the additional characteristic that it represents the turning point of the zone so that monatomic steps and terraces can be interchanged in the step/terrace notation. Thus, this surface represents one where there is the same number of step and terrace sites. We maintain the aforementioned step-terrace notation based on the electrochemical behavior described previously for platinum surfaces in this zone [19]. In addition, we also investigated the effects of chloride and bromide since it is well known that their presence can dramatically affect the upd of copper on the platinum basal single crystals [2,9,11,12,14-16]. Of particular interest will be to test if the

deposition of copper occurs preferentially on the terraces or on the steps as well as the competition between the anions and copper for these surface sites.

EXPERIMENTAL

Apparatus and cells have been described elsewhere [9]. All potentials were measured against a Ag/AgCl (sat. NaCl) reference electrode. A coiled platinum wire was used as a counterelectrode. All experiments were made at room temperature.

The platinum single crystal electrodes used in these experiments were prepared following Clavilier's technique described in reference 20. Before each experiment, the single crystal electrode was subjected to a high temperature treatment [21] and then quenched in ultrapure water. In the case of both Pt(100) and Pt(311), the electrode was cooled in a mixture of hydrogen and nitrogen [19,22] since this minimizes the presence of surface defects. Then, a protective droplet of ultrapure water was formed by immersion of the sample into water saturated with both gases.

Solutions were prepared using ultrapure water (18 MOhms Millipore Milli-Q water). Aqueous acid solutions were prepared from high-purity (ULTREX) sulfuric acid. Copper ion solutions were prepared by dissolution of $CuSO_4.5H_2O$ (Aldrich Gold Label 5N5) in sulfuric acid solutions. Chloride and bromide containing solutions were prepared by dissolution of NaCl and NaBr (Aldrich Gold Label) in 0.1M H_2SO_4 solution.

Prior to introduction into the electrochemical cell, the solutions were degassed for at least 20 min with prepurified nitrogen gas which was passed through hydrocarbon and oxygen traps (MG industries).

RESULTS and DISCUSSION

1. Voltammetric characteristics of a Pt(311) electrode in acidic solutions containing chloride and bromide.

Fig. 1 shows cyclic voltammograms for the Pt(311) electrode in contact with a 0.1 M H_2SO_4 solution in the presence and absence of chloride and bromide. For the case of sulfuric acid

solutions, and as can be ascertained from the figure, two adsorption regions can be distinguished. There is a broad peak below -0.05 V corresponding to the adsorption of hydrogen on the (111) terrace sites and a very sharp and reversible peak at +0.02 V corresponding to the adsorption/desorption of hydrogen coupled with the desorption/adsorption of sulfate/bisulfate on the (100) steps [23]. Such behavior has been previously reported [19]. The adsorption of the anions on the steps is favored, not only because of the higher coordination and possibility of bonding of these sites, but also because of the lowering of the work function of this step sites relative to the terrace sites [24].

The presence of 1×10^{-3} M NaCl affects the (111) and (100) sites in a distinct fashion. The peak corresponding to the adsorption on (111) sites remains unaffected, providing additional evidence that only hydrogen is involved in this process. In contrast, the presence of chloride has a strong influence on the adsorption processes at the steps. These are shifted towards more negative potentials, indicating that, as expected, the adsorption of chloride is stronger than that of bisulfate. A qualitatively similar behavior has been observed for these stepped sites in presence of oxalic acid. That is, there is a shift of the peak corresponding to the steps towards more negative potentials [25].

The effects of the presence of 1×10^{-3} M NaBr are similar to those described for the case of NaCl. The main difference is the larger shift towards negative potentials of the peak corresponding to the adsorption/desorption processes on the steps. This is a reflection of the fact that bromide is more strongly adsorbed than chloride.

The total voltammetric charge density corrected for the apparent double layer, amounts to 287 μC/cm^2 in the absence of chloride and bromide. In the case of the chloride containing electrolyte, the total charge density is 299 μC/cm^2. Finally, when 1×10^{-3} M bromide is present in the solution, the total charge amounts to 250 μC/cm^2. In this latter case it is difficult to distinguish between the processes due to the adsorption/desorption on the steps and on the terraces since both processes take place in the same potential region.

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A point that remains unexplained is why the voltammetric profile corresponding to the steps is much sharper in the case of bisulfate than in the case of the halides. This could be due to the existence of cooperative adsorption inducing a hydration network on the steps in the former case. However, we have no direct experimental evidence in support of this.

2. The underpotential deposition of copper on Pt(311).

Fig. 2 shows the steady state voltammetric profile (v=50 mV/s) for a Pt(311) electrode in a 0.1 M H_2SO_4 solution containing $1x10^{-3}$ M copper. On the positive-going sweep, two stripping peaks can be observed at potential values of +0.50 and +0.56 V. As can be seen, the peak at +0.56 V corresponds to a process much more reversible than that at +0.50 V whose counterpeak in the negative-going sweep is centered at +0.15 V. Lowering of the sweep rate did not significantly affect the shape of the voltammetric profile. However, the peak at +0.15 V was shifted towards positive potentials. This is the expected behavior when lowering the sweep rate. However, reversible behavior was not attained at sweep rates as low as 2 mV/s. It should be mentioned that the appearance of a small peak at +0.11 V represents the onset of the bulk deposition of copper.

The charge density in the positive going sweep amounts to 508 $\mu C/cm^2$. If we correct for the apparent double layer contribution and consider only the two well defined stripping peaks, this charge is equal to 462 $\mu C/cm^2$. From these, 226 correspond to the first stripping peak and 236 to the second. As can be seen, both charge densities are almost equal. This points to the possibility that one peak corresponds to the stripping of copper deposited on the (111) sites and the other to the stripping of copper deposited on the (100) sites, since the number of both types of sites is equal for an ideal Pt(311) surface [19].

In order to establish this, additional experiments were performed at a lower concentration of copper (10 μM). The use of such a low concentration is helpful since it allows for the deposition of sub-monolayer amounts of copper with relative ease. In addition, it allows for an assessment of the voltammetric peaks in the hydrogen adsorption/desorption region while the surface is covered with sub-monolayer amounts of copper. The results are presented in Fig. 3.

Curves marked with 1 in this set of figures are the steady state voltammograms recorded in this solution at 50 mV/s. The voltammetric features are quite similar to those presented in Figure 1 (solid line) obtained in the absence of copper. The main difference is the existence of a small peak centered at +0.45 V corresponding to the stripping of the small amount of copper accumulated during one voltammetric cycle. Curves marked with 2 correspond to the voltammetric profile (one cycle between -0.21 and 0.20 V) obtained after holding the potential at the negative limit (-0.21 V) for different times ranging from 30 s to 10 min. In this way, the deposition of different and controlled amounts of copper on the surface is achieved. As can be clearly seen, the peaks corresponding to the adsorption processes taking place on the platinum sites progressively diminish. It is worth noting that the voltammetric peaks corresponding to the adsorption/desorption processes occurring at the (100) steps are broadened but the voltammetric charge density under these peaks is not affected to a great extent. Curves 3 correspond to the stripping of the accumulated copper. The amount of charge associated with the stripping of copper (curve 3) increases with the length of time for which the potential was held at -0.21 V. Data are summarized in Table I where two charge density ratios are presented. r_1 is the ratio between the charge density corresponding to the sharp peak at +0.24 V after and before the deposition of copper. This could be interpreted as the fraction of step sites free of copper. r_2 corresponds to the same ratio for the broad peaks below -0.05 V. This would correspond to the fraction of terrace sites free of copper. The charge under the stripping peak(s) of the submonolayer of copper is also presented. This charge is only corrected for the apparent double layer. It is evident from the analysis of the data presented in this table (and from Fig. 3) that copper adatoms are preferentially adsorbed on the terraces as the value of r_1 is systematically higher than that of r_2. It is worthwhile remarking that the appearance of a second stripping peak at less positive potentials coincides with the existence of an important blocking of the steps.

This set of data allows us the unambiguous assignment of the two peaks observed during the stripping of the monolayer of copper adsorbed on Pt(311). The peak at +0.50 V corresponds to the desorption of copper from the steps ((100) sites) and the second one to the desorption from the

terrace (111) sites. It can be concluded that copper is preferentially adsorbed and is more stable on the terraces than on the steps. This behavior is striking, since step sites are expected to be the preferred ones in the adsorption of adatoms due to their higher coordination. This tendency has been observed with a number of irreversibly adsorbed adatoms including Bi, As and Te [26-29]. The main difference between copper and the other adatoms studied is the character of deposition/dissolution process which is reversible in the case of copper adatoms. Therefore, specifically adsorbed anions could compete more effectively for these adsorption sites. Thus, the apparently less favored adsorption of copper on the steps would be actually due to a preferred adsorption of anions so that cation electrosorption/desorption would, in effect, be controlled by the desorption/adsorption of the anions.

The desorption of a partial second layer of copper is reflected in Fig. 3f where the appearance of a small irreversible peak in the positive-going sweep centered at 0.01 V is clearly observed.

It is important to point out that after the stripping of copper, the voltammetric profile is virtually the same as presented in curves 1. That is to say, the adsorption/desorption of copper does not induce neither reconstruction nor the loss of the long-range order of the surface. This, however, is not the case for the adsorption of several irreversibly adsorbed adatoms or carbon monoxide [30] on this kind of surface. We take advantage of this experimental result to infer structural data.

A question that needs to be addressed is the stability of the copper adatoms on steps and terraces in relation with the stability on the platinum basal planes of the same symmetry. It should be taken into account that the (311) surface consists of parallel and alternate long rows of (100) and (111) sites. This means that the adsorbate-adsorbate interactions should occur only in one direction and not in two as would be the case on the smooth Pt(100) and Pt(111) surfaces. Such a comparison is presented in fig. 4 which shows the voltammetric profiles for Pt(100), Pt(311) and Pt(111) electrodes in the same solution and under identical voltammetric conditions. The voltammetric profile for copper upd on Pt(111) in sulfuric acid electrolyte is well-known with the

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coulometric charge for desorption of a monolayer being about 490 $\mu C/cm^2$. In the case of the Pt(100) electrode only one stripping process is present for sweep rates ranging from 5 to 100 mV/s. The charge involved in this case is 420 $\mu C/cm^2$. With respect to the deposition process, it is characterized by the existence of two well-resolved peaks at +0.46 and +0.34 V. The amplitude of these two peaks is a strong function of the sweep rate. At lower scan rates, the peak at +0.46 V shifts towards more negative potentials and finally, only one peak can be distinguished. It is remarkable that copper is more stable on Pt(100) that on Pt(111). Relative to the behavior on the basal planes, we notice that on the Pt(311) surface, deposition on the terrace (111) sites is slightly favored (peak is shifted towards positive potentials) whereas deposition on steps (100) sites is significantly destabilized (peak is drastically shifted towards negative potentials).

Taking into account that copper is not irreversibly adsorbed, one of the main reasons producing the changes in the potentials of adsorption and desorption could be the competitive adsorption/desorption of anions, as pointed out above.

In this respect, it is known that the adsorption of anions on (111) terraces is dependent on their width, with stronger adsorption taking place on wider terraces. This can be concluded in the case of sulfuric acid solution by the shift of the so-called unusual adsorption states, due to the adsorption/desorption of bisulfate [31], towards positive potentials as the width of the terraces decreases [19]. In the case of Pt(311), bisulfate anions are less strongly adsorbed on the (111) terrace sites than in the case of a well ordered Pt(111) electrode. Thus, the adsorption of copper on (111) sites can take place at more positive potentials, as observed in fig. 4.

In contrast, in the case of (100) sites (step sites), the adsorption of anions is enhanced with respect the behavior of the well-ordered Pt(100) electrode, thus disfavoring the adsorption of copper adatoms or favoring their desorption. Based on this behavior, one would predict a significant shift of the copper stripping peak towards negative potentials as was indeed observed.

From these results it is clear that one can deliberately and selectively decorate a surface (step or terrace sites), thus allowing for the preparation of uni-dimensional structures.

3. The underpotential deposition of copper on Pt(311) in the presence of chloride.

Fig. 5 shows the steady state voltammetric profile (v=5 mV/s) for a Pt(311) electrode in a 0.1 M H_2SO_4 solution containing 1×10^{-3} M of both copper and NaCl. Four stripping peaks can be distinguished at +0.285, +0.340, +0.420 and +0.495 V. All peaks exhibited reversible behavior at 5 mV/s. The total charge involved in these processes was 460 $\mu C/cm^2$. Of these, 290 $\mu C/cm^2$ would correspond to the two peaks at lower potentials (measured between +0.18 and +0.38 V) and 170 $\mu C/cm^2$ to the two other peaks at higher potentials. It is also interesting to note the existence of a couple of small reversible steps at about +0.105 V.

In order to identify these peaks in terms of the site of deposition on the surface, we carried out some experiments at low copper concentration and relatively high sweep rates (v=50 mV/s). As mentioned earlier, this allows for a progressive and selective blockage of the surface. Thus, submonolayer deposition of copper can be controlled so that variations in the voltammetric profile as a function of coverage can be observed. Fig. 6a shows the first voltammetric profile, up to +0.40 V, obtained in the case of a solution containing 1×10^{-5} M copper and 1×10^{-3} M NaCl. Some important points are noted. A stripping peak due to the small quantity of copper adatoms accumulated during one cycle is apparent at +0.35 V. In addition, a pair of peaks at about 0.00 V is still present. These peaks correspond to the adsorption of hydrogen and chloride on the steps. Thus we can conclude that initially, the step sites are free of copper. In contrast, the lower potential region between -0.21 and -0.10 V shows a significant extent of blockage relative to the blank voltammogram obtained in the case of the absence of copper (see fig. 1), suggesting that as in the absence of chloride , terraces are preferentially blocked. It is noteworthy that the presence of copper adatoms on the adjacent (111) sites causes a shift towards positive potentials of the peak linked to the steps. This can be interpreted as an destabilization of the chloride anions adsorbed on the steps. This could suggest that chloride is mostly discharged when adsorbed on the platinum surface. Thus the interactions between a partially charged copper [9,15,16,32-35] and chloride adspecies may not necessarily be attractive.

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When the potential window is closed, the positive potential limit being reduced to +0.20 V, a blockage of the steps takes place as can be seen by the disappearance of the peak at 0.00 V. In addition, when the surface is completely blocked, a small irreversible peak appears at +0.08 V, corresponding to the desorption of a partial second layer of copper.

Fig. 6b shows the effect of opening the window up to +0.40 V once the surface is completely covered by copper. The first sweep shows the appearance of two stripping peaks at +0.27 and +0.32 V. These peaks would correspond to those observed in Fig. 5, obtained under conventional UPD conditions, at +0.285 and +0.34 V, respectively. During the subsequent voltammetric cycles, the main effects are the progressive diminution of the stripping peaks and a simultaneous partial recovery of the adsorption states corresponding to the steps. From these experiments it can be concluded that these two peaks are due to the desorption of copper adsorbed on the steps.

The peak at +0.27 V disappears faster than the one at +0.32 V. We cannot rule out the possibility that this peak could be due to the adsorption of chloride on top of the copper adatoms adsorbed on the steps. A similar behavior has been proposed in the case of the copper adlayer on Pt(111) [11,12,15].

Upon further opening of the potential window to +0.60 V (Fig. 6c) two new stripping peaks appear at +0.46 V and +0.50 V and these steadily decrease with successive cycles. These stripping peaks correspond to those observed at +0.42 V and +0.495 V in the experiment presented in Fig. 5. The small differences between the peak potentials could be due to the different experimental conditions (copper concentrations, sweep rates) used in both cases.

An important feature observed during this experiment is the progressive recovery of the adsorption capability of the terraces as can be see from the appearance of broad voltammetric peaks in the potential region below -0.10 V. Based on this evidence, we can ascribe the peaks at +0.46 and +0.50, during the positive going sweep, to the stripping of the copper previously adsorbed on the terraces. It is clear that upon stripping, there is also a total recovery of the peaks at 0.00 V corresponding to the adsorption/desorption processes on the step sites whose voltammetric profile

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becomes similar to that obtained in the absence of copper. This would suggest some kind of interaction between the terrace and the step sites.

Thus, the two peaks at lower potentials during the upd of copper correspond to the desorption of copper from the steps whereas the other two at higher (more positive) potentials would correspond to the desorption from the terraces. This behavior is very similar to that aforementioned in the absence of chloride.

It is interesting to point out that if the copper previously adsorbed on the terraces is not stripped, then the adsorption/desorption processes of copper on the (100) sites are much better defined as can be seen in fig. 7. In this figure, the solid line corresponds to the steady state voltammetric profile obtained when the positive potential limit is at +0.40 V. It is also worth pointing to the appearance of a couple of small reversible peaks at +0.14 V. Based on the experiments carried out at a low concentration of copper, we tentatively ascribe these small peaks to the initial stages of formation of a second monolayer. If after recording this profile, the window is opened, the stripping of the copper adsorbed on the terrace (111) sites is again observed, but the voltammetric peaks are less defined, supporting the previous suggestion of an interaction between terrace and step sites.

If one compares the potentials at which the desorption of copper takes place in the absence and presence of chloride (Figs. 2 and 5), it is apparent that the copper on the (111) sites is not greatly affected by the presence of chloride, indicating that the interaction of chloride with these extremely narrow (111) terrace sites is not as strong as in the case of a well-ordered Pt(111) electrode. In contrast, the desorption process on the step sites is shifted towards more negative potentials indicating that copper is less stable on the surface due to the competition of the anions (chloride) for the adsorption sites.

By comparing the upd of copper in chloride-containing electrolytes on Pt[2(111)x(100)], Pt(100) and Pt(111) (fig. 8), one can observe a behavior similar to that in the case of the absence of chloride. The voltammetric behavior for the Pt(111) electrode is well known showing two sharp

peaks in both the positive and the negative going sweeps [9,11]. In this case, the coulometric charge due to the desorption of a monolayer is equal to 470 $\mu C/cm^2$ [9].

In the case of the Pt(100) electrode only one stripping (+0.45 V) and one deposition peak (+0.40 V) can be observed in the presence of chloride. The amount of charge under the stripping peak is 450 $\mu C/cm^2$. This result is at odds with that previously reported by Markovic and Ross [12] where a significant decrease of this stripping charge was observed when different amounts of chloride were added to the solution. Nevertheless, the appearance of a well-defined peak prior to the deposition of copper can be clearly distinguished as reported by these authors. We tentatively ascribe this peak at +0.02 V to the formation of a second layer prior to the bulk deposition of copper. The formation of a second layer, prior to bulk deposition has been observed for the upd of silver on platinum single crystal electrodes [35-38].

In terms of the behavior of the (100) and (111) sites contained in the Pt(311) surface, the same effects and explanations expounded in the case of the chloride free solution are applicable. The copper adsorbed on the step (100) sites is much less stable than on the Pt(100) surface whereas the copper adsorbed on terraces (111) is not greatly affected relative to the Pt(111) surface. This can be explained in terms of the strong interactions between chloride and step sites as expounded above for the case of sulfate/bisulfate anions.

4. The underpotential deposition of copper on Pt(311) in the presence of bromide.

Fig. 9 shows the steady state voltammetric profile for a Pt(311) electrode in a 0.1 M H_2SO_4 solution containing 1×10^{-3} of both copper and NaBr (v = 5 mV/s). Two stripping peaks can be distinguished at +0.24 and +0.38 V. During the negative-going sweep, two peaks are also apparent at +0.32 and +0.24 V. In order to identify the adsorption states to which these peaks correspond, experiments at low copper concentration were performed as in the preceding cases. Fig. 10a, curve 1, shows the steady state voltammetric profile for a Pt(311) electrode in the presence of 1×10^{-3} M bromide and 1×10^{-5} M copper. This profile is very similar to that obtained in the absence of copper (Figure 1) with the difference being the appearance of a small peak at

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about +0.50 V corresponding to the stripping of the copper accumulated during one voltammetric cycle. Curve 2 presents the voltammetric cycle in the lower potential range obtained after holding the potential at -0.21 V for 30 s. As can be seen, the subsequent voltammogram shows a significant blockage of the voltammetric charged linked to terrace (111) sites. This is apparent from the diminution of the peaks at -0.21 V. It is worth noting that the diminution in the charge ascribed to the steps indicates that in this case the terraces are also preferentially blocked.

The displacement of the peak corresponding to the steps towards more positive potentials suggests that, when copper is present on the terrace (111) sites, the adsorption of bromide is disfavored as was found in the case of chloride. Only one peak due to the stripping of copper can be observed at about +0.46 V. If similar experiments are carried out after different time periods at -0.21 V, the peaks corresponding to the steps also diminish and correspondingly the stripping of the copper shows new shoulders (fig. 10b) at lower potentials. This suggests that the first oxidative peak of the upd of copper in the presence of bromide is due to the desorption of adatoms from the steps and that the second is due to the desorption of copper from the terraces as seen in the two previous cases.

In figure 10c, we can see a similar set of curves after holding the potential at -0.21 V for 10 min. It is interesting to note that even after such an extended time period, the steps are not completely blocked. Nevertheless, the formation of a second layer, or the onset of bulk deposition, is apparent as can be deduced from the stripping voltammetric profile that presents a prominent new stripping peak at +0.04 V. This could be a consequence of the greater stability of bromide on the step sites on the platinum surface relative to chloride or sulfate/bisulfate. Such an interaction could make the adsorption of additional amounts of copper on the first layer of copper adatoms to be more favorable than the direct adsorption on the platinum sites due to the competition with the adsorbed bromide. Although this is somewhat speculative, it is consistent with the known strength of adsorption of anions.

As in the case of the other two anions, we can compare the voltammetric profiles obtained under the same conditions for Pt(311), Pt(111) and Pt(100) (fig. 11). In the case of the Pt(111)

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electrode, the typical voltammetric profile is observed, with two peaks in both the stripping and the deposition of copper as described previously [9,11]. The total charge density in this case is equal to 570 $\mu C/cm^2$, which is a strikingly high value. In the case of the Pt(100) electrode, only one stripping peak is observed at +0.53 V. As in the other cases, the stability of the copper adatoms on this surface is greater. The charge involved during the desorption on the Pt(100) surface amounts to 420 $\mu C/cm^2$. It is worth remarking that for this surface, the process is rather irreversible. If we compare this profile to that obtained in the presence of chloride, we observe a shift of the stripping peak towards positive potentials. This is a striking behavior, since even though bromide is more strongly adsorbed than chloride, the copper adlayer is not destabilized. A similar behavior is again observed for the adsorption of copper on terraces and steps and such behavior can again be understood by taking into account the strong interaction between anions and steps.

CONCLUSIONS

The underpotential deposition of copper on Pt(311)= Pt[2(111)x(100)] has been studied and we find that the deposition/stripping processes occur in two stages related to the presence of (100) steps and (111) terraces. We find that copper is more stable when adsorbed on the terraces relative to the steps. We ascribe this observation to a greater extent of interaction between the anions and the step (100) sites, where competitive adsorption of anions produces a weakening in the strength of adsorption of copper adatoms on the step sites. The unambiguous identification of the specific sites of adsorption was only possible by using low concentrations of copper as well as relatively high sweep rates in order to monitor this selective adsorption as a function of coverage.

We have been able to show that on this kind of surface, copper adatoms can be selectively adsorbed at specific sites allowing for the preparation of uni-dimensional structures.

The presence of halides (Cl⁻, Br⁻) has a strong influence on the copper deposition/stripping processes, resulting in additional voltammetric features. However as in the absence of halides, deposition on terrace (111) sites was favored over deposition on step (100) sites. Again, it is thought that the competitive adsorption of the anions is responsible for this effect.

We have also shown that successive cycles of adsorption/desorption do not modify the structure of the surface, thus allowing for a structural interpretation of the results.

Finally, we find evidence that suggests the formation of a second copper layer prior to bulk deposition of copper on Pt(100). It is thought that the formation, at underpotentials, of this second layer could be induced by the presence of halides in the solution.

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TABLE I

r_1: ratio between the charge density corresponding to the sharp peak at +0.24 V after and before the deposition of copper; r_2: ratio between the charge density corresponding to the broad peak below -0.05 V; Q: net stripping charge density corrected for the apparent double layer.

Holding Time at -0.21 V (s)	r_1	r_2	Q ($\mu C/cm^2$)
30	0.92	0.76	103
60	0.73	0.47	155
120	0.67	0.20	260
180	0.53	0.00	284
300	0.43	0.00	304
600	0.00	0.00	446

FIGURE CAPTIONS

Fig. 1. Voltammmetric profiles for the Pt(311) electrode in the absence (solid line) and the presence of either 1×10^{-3} M of chloride (dashed line) and bromide (dotted line). v=50 mV/s.

Fig. 2. Voltammogram corresponding to the upd of copper on Pt(311). Test electrolyte: 0.1 M H_2SO_4 + 1×10^{-3} Cu^{2+}. v=50 mV/s.

Fig. 3. Voltammetric profiles corresponding to experiments with a low concentration of copper: 1×10^{-5} M. **Curves 1.** Steady-state profile. **Curves 2.** Voltammogram in the lower potential region after holding the potential at -0.21 V during different times. **Curves 3.** Stripping of the copper accumulated during the previous stage. Times of holding at -0.21V: **a.** 30 s. **b.** 1 min. **c.** 2 min. **d.** 3 min. **e.** 5 min. **f.** 10 min. v=50 mV/s.

Fig. 4. Voltammetric profiles for the upd of copper on different substrates. 0.1 M H_2SO_4 + Cu^{2+} 1×10^{-3} M. Solid line: Pt(100). Dashed line: Pt(111). Dotted line: Pt(311). v=50 mV/s.

Fig. 5. Steady state voltammogram corresponding to the upd of copper on Pt(311). Test electrolyte: 0.1 M H_2SO_4 + 1×10^{-3} NaCl + 1×10^{-3} Cu^{2+}. v=5 mV/s.

Fig. 6.a. Successive voltammetric profiles for a Pt(311) electrode over different potential ranges. Test Electrolyte: 0.1 M H_2SO_4 + 1×10^{-3} NaCl + 1×10^{-5} Cu^{2+}. v=50 mV/s. **b.** Effect of opening the potential up to 0.40 V. **c.** Effect of opening the potential up to 0.60 V.

Fig. 7. Steady state voltammogram corresponding to the upd of copper on Pt(311) upon closing the potential window to +0.40 V and opening the window up to +0.60 V. Test electrolyte: 0.1 M H_2SO_4 + 1×10^{-3} NaCl + 1×10^{-3} Cu^{2+}. v=5 mV/s.

Fig. 8. Voltammetric profiles for the upd of copper on different substrates. 0.1 M H_2SO_4 + $1x10^{-3}$ M NaCl + Cu^{2+} $1x10^{-3}$ M. Solid line: Pt(100). Dashed line: Pt(111). Dotted line: Pt(311). v=5 mV/s.

Fig. 9. Steady state voltammogram corresponding to the upd of copper on Pt(311). Test electrolyte: 0.1 M H_2SO_4 + $1x10^{-3}$ NaBr + $1x10^{-3}$ Cu^{2+}. v=5 mV/s.

Fig. 10. Voltammetric profiles corresponding to experiments with a low concentration of copper: $1x10^{-5}$ M in the presence of $1x10^{-3}$ M NaBr. **Curves 1.** Steady-state profile. **Curves 2.** Voltammogram in the lower potential region after holding the potential at -0.21 V during different times including the stripping of the copper accumulated. Times of holding: **a.** 30 s. **b.** 2 min. **c.** 10 min. v=50 mV/s.

Fig. 11. Voltammetric profiles for the upd of copper on different substrates. 0.1 M H_2SO_4 + $1x10^{-3}$ M NaBr + Cu^{2+} $1x10^{-3}$ M. Solid line: Pt(100). Dashed line: Pt(111). Dotted line: Pt(311). v=5 mV/s.
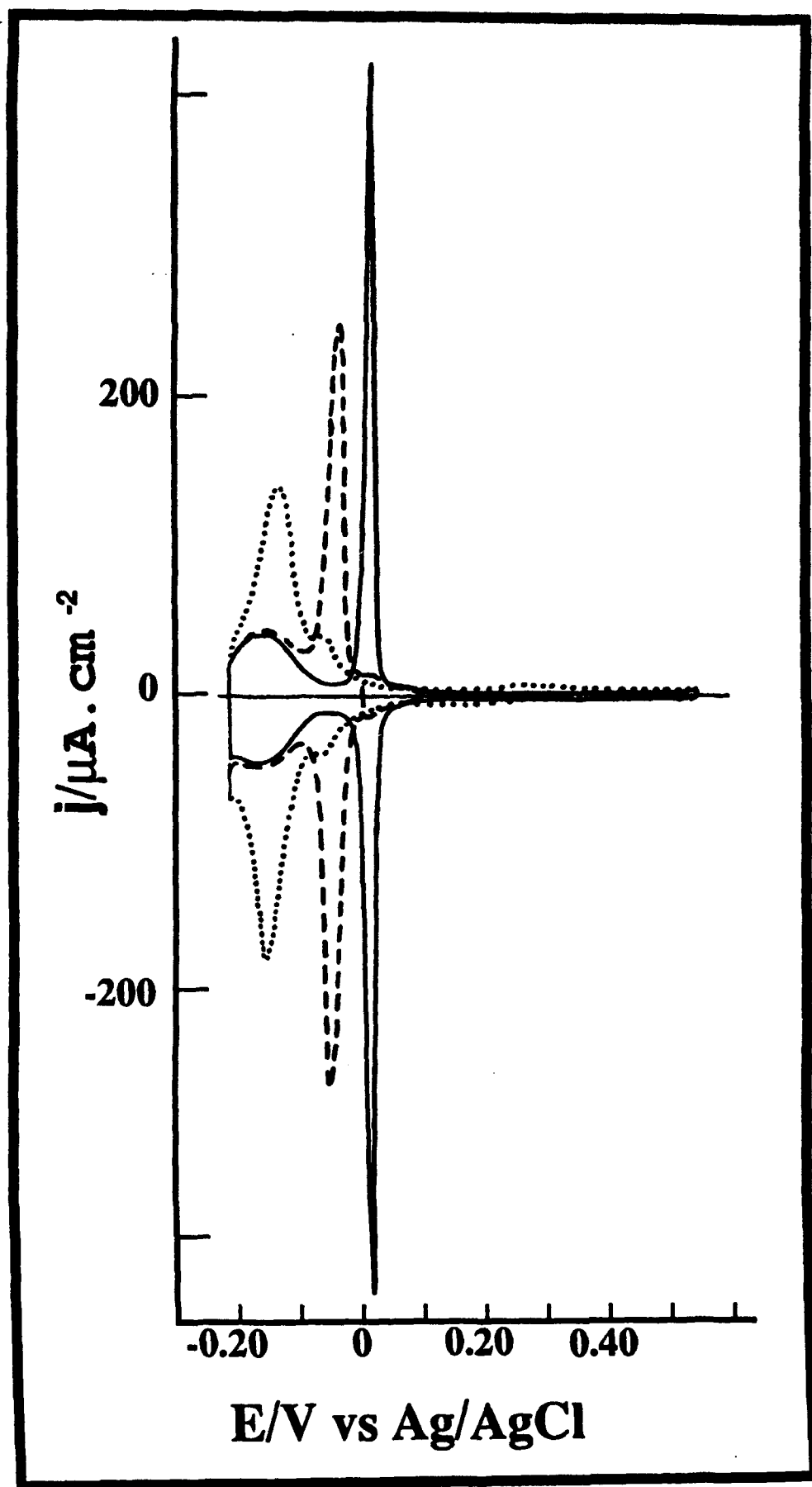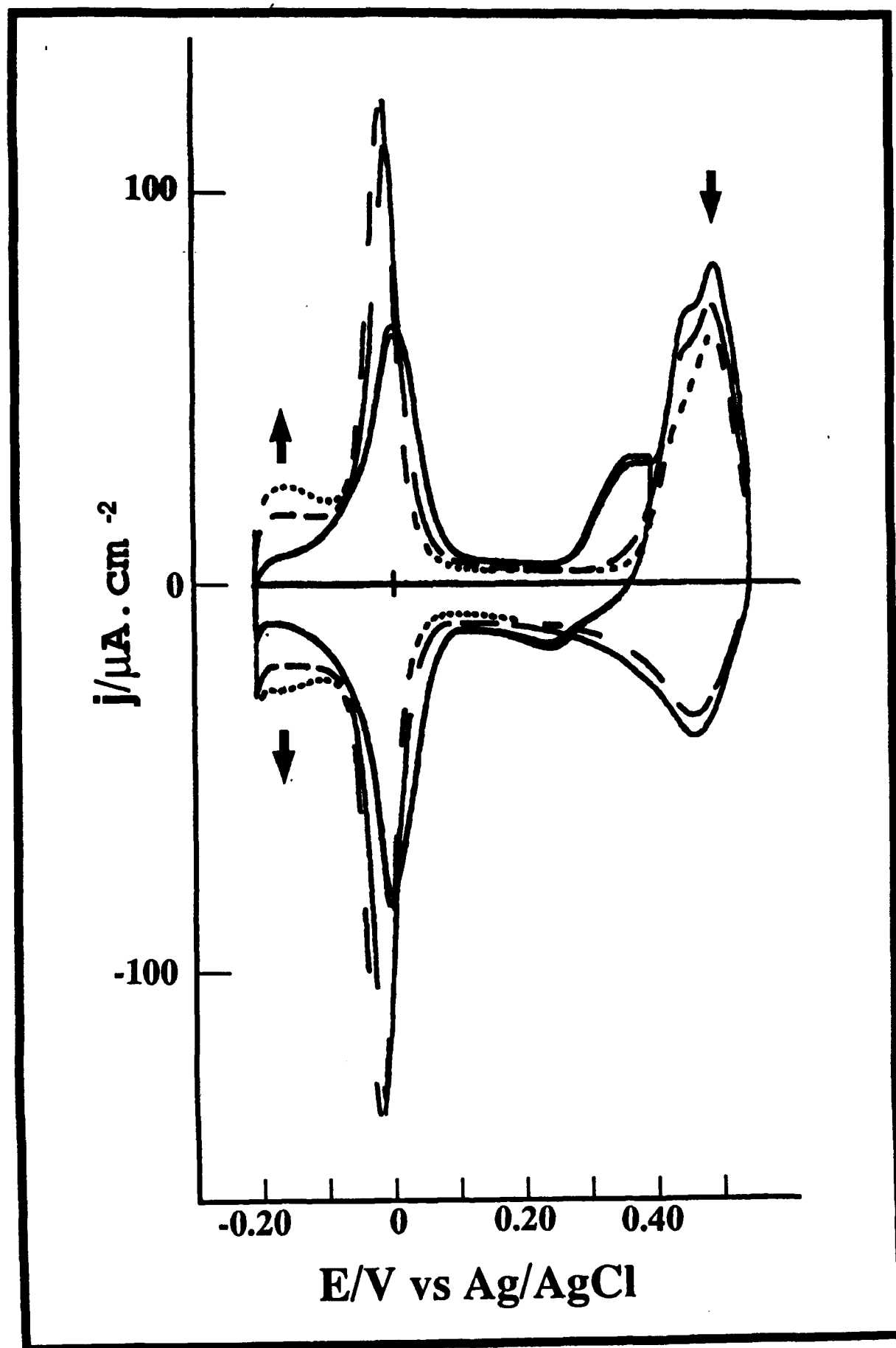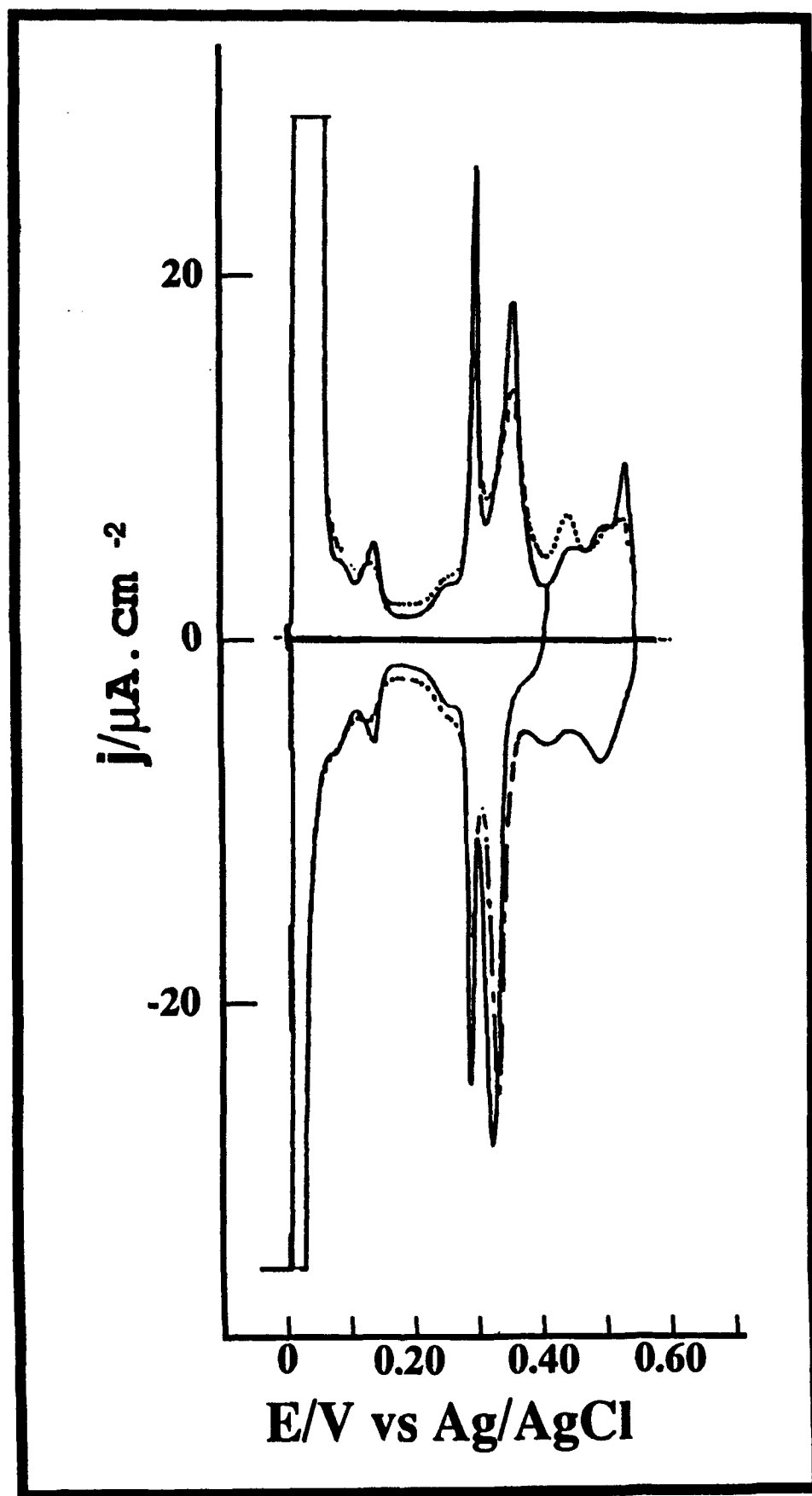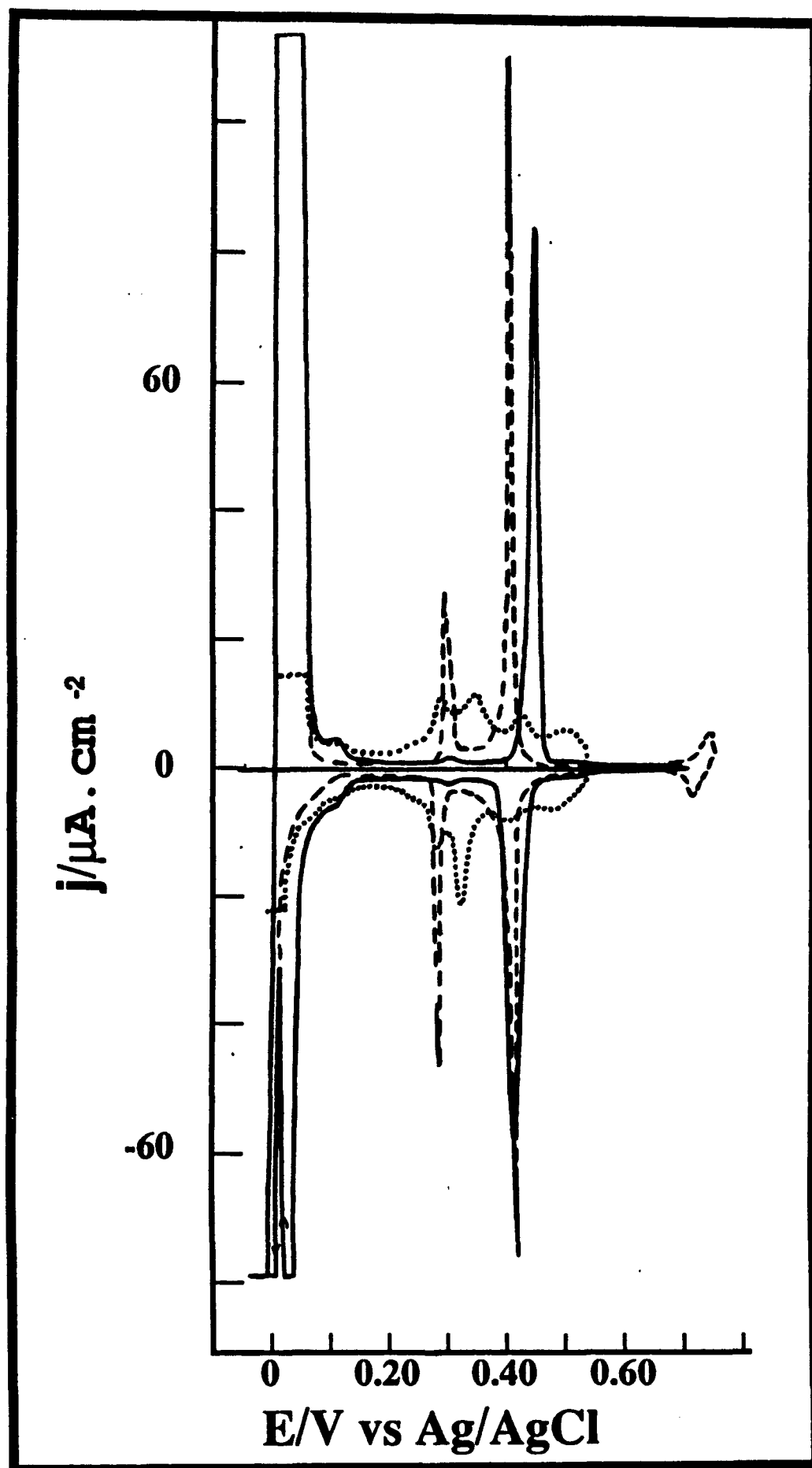
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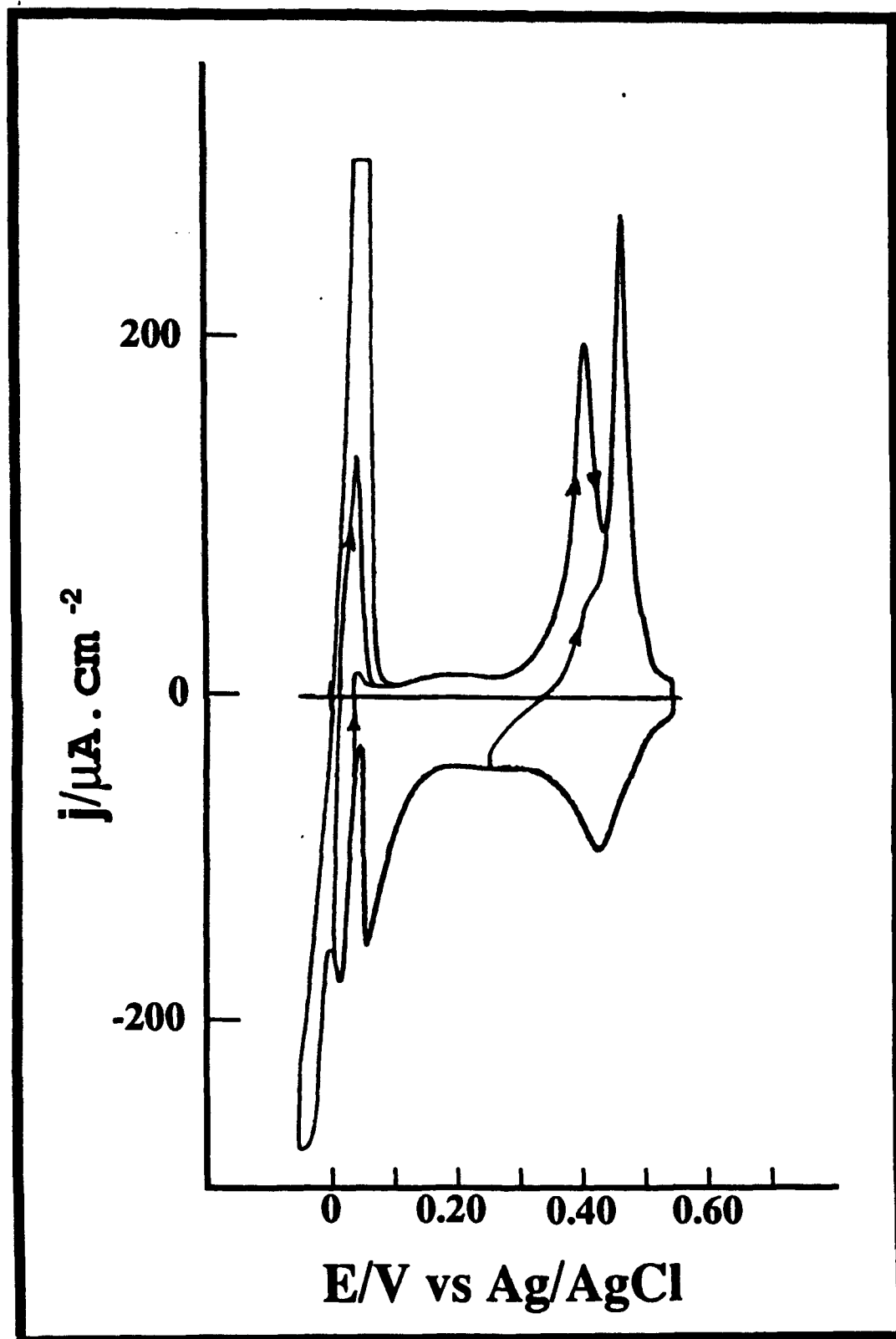
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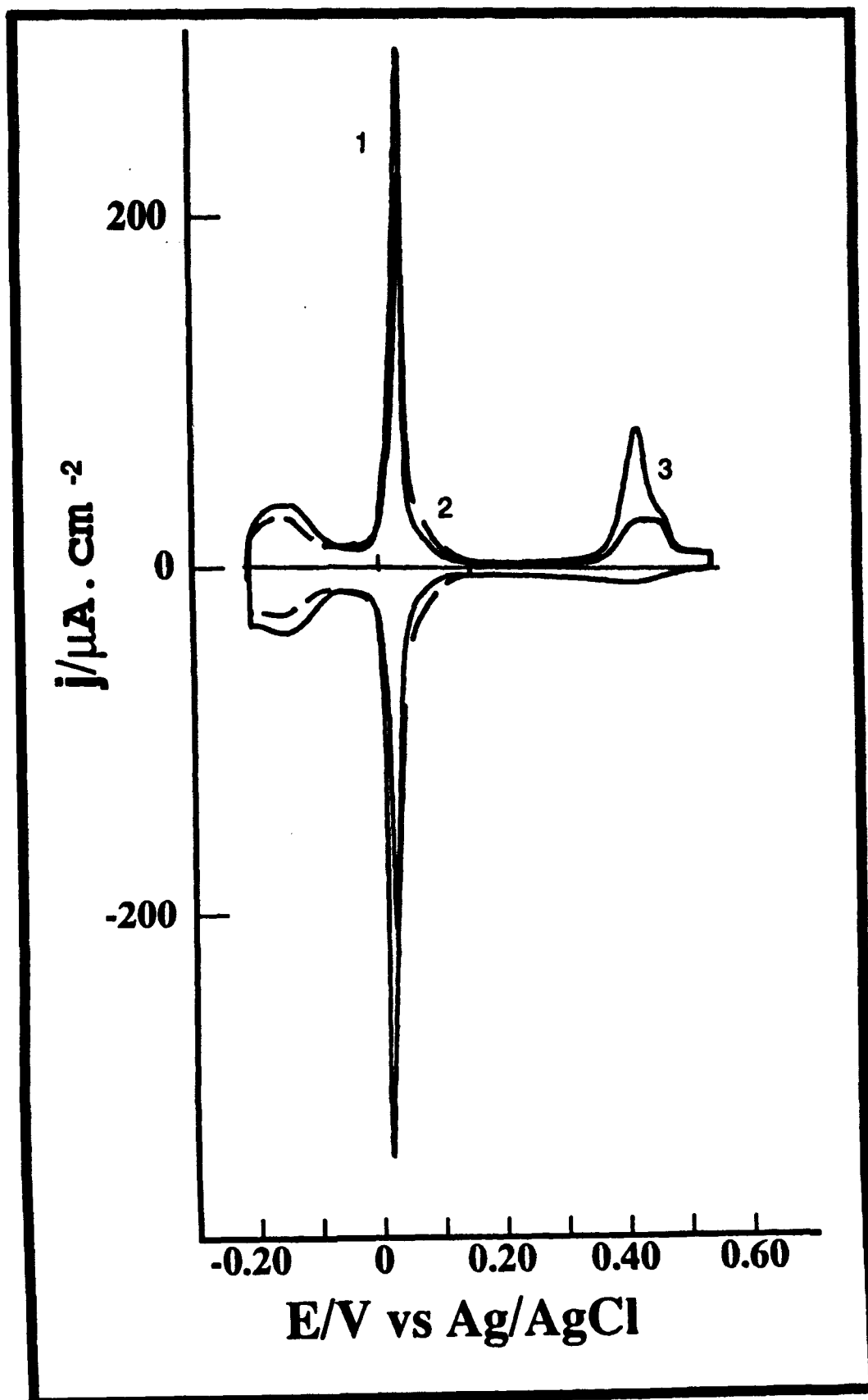
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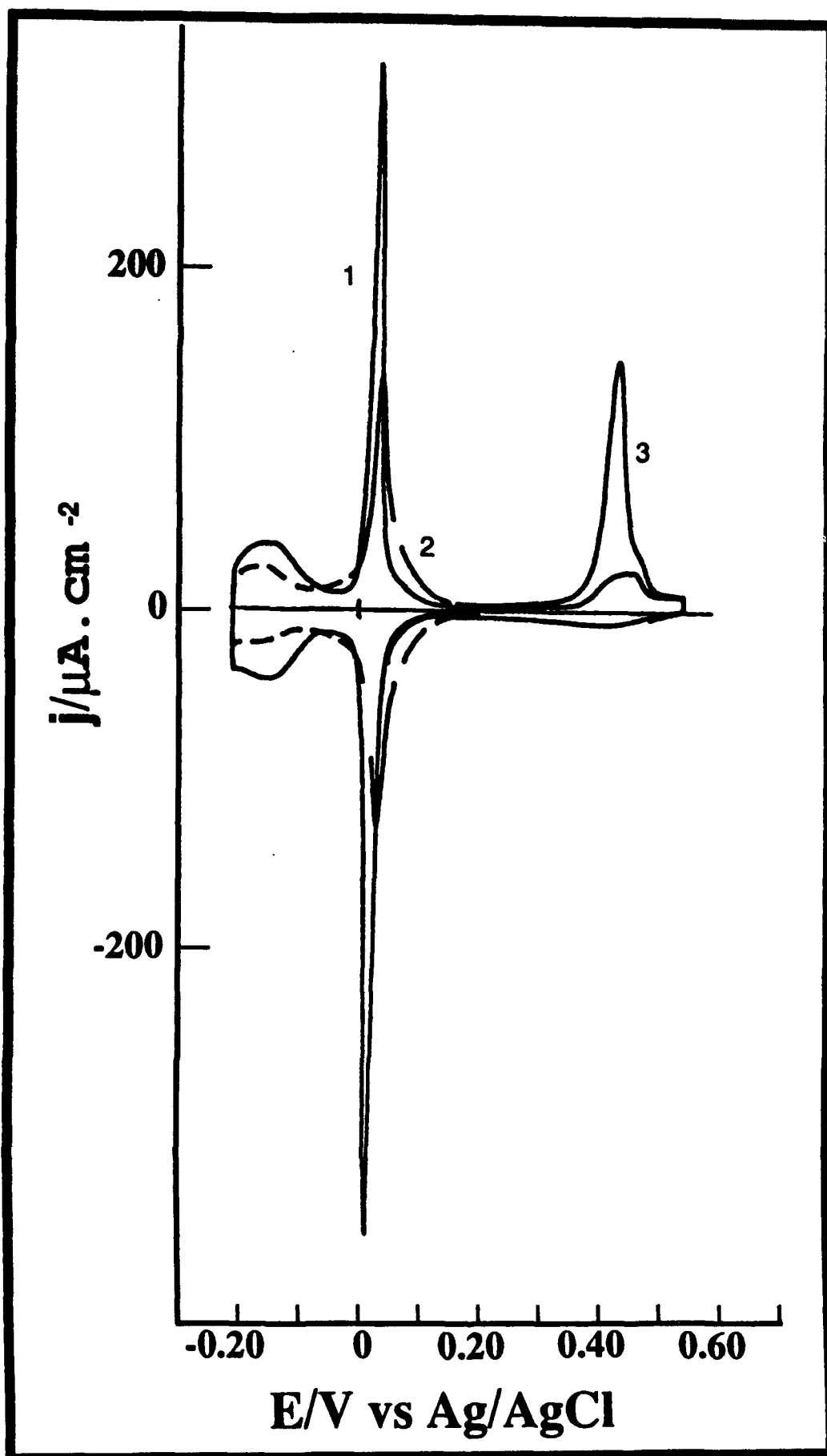
Figure 3b

Figure 3c

Figure 36

31
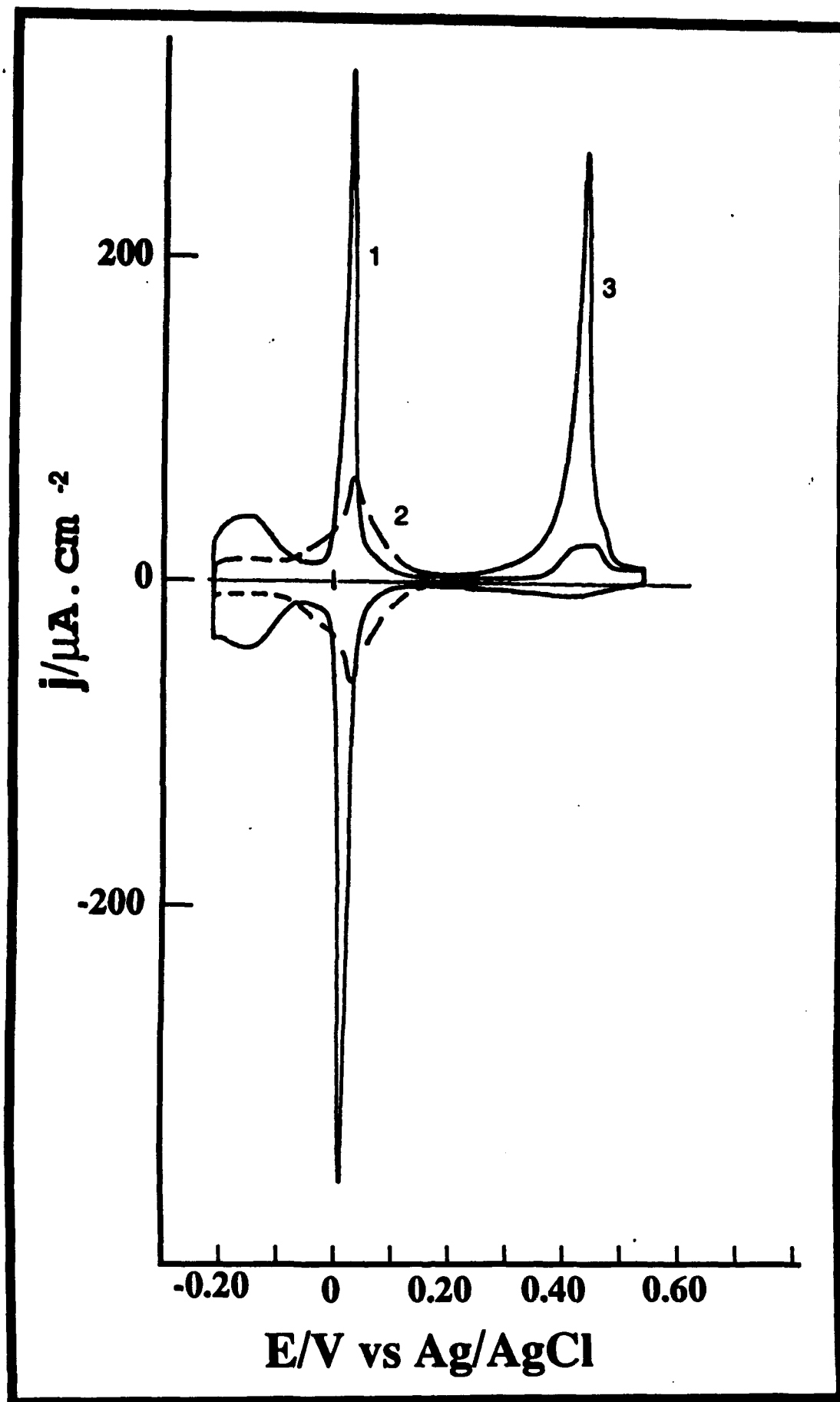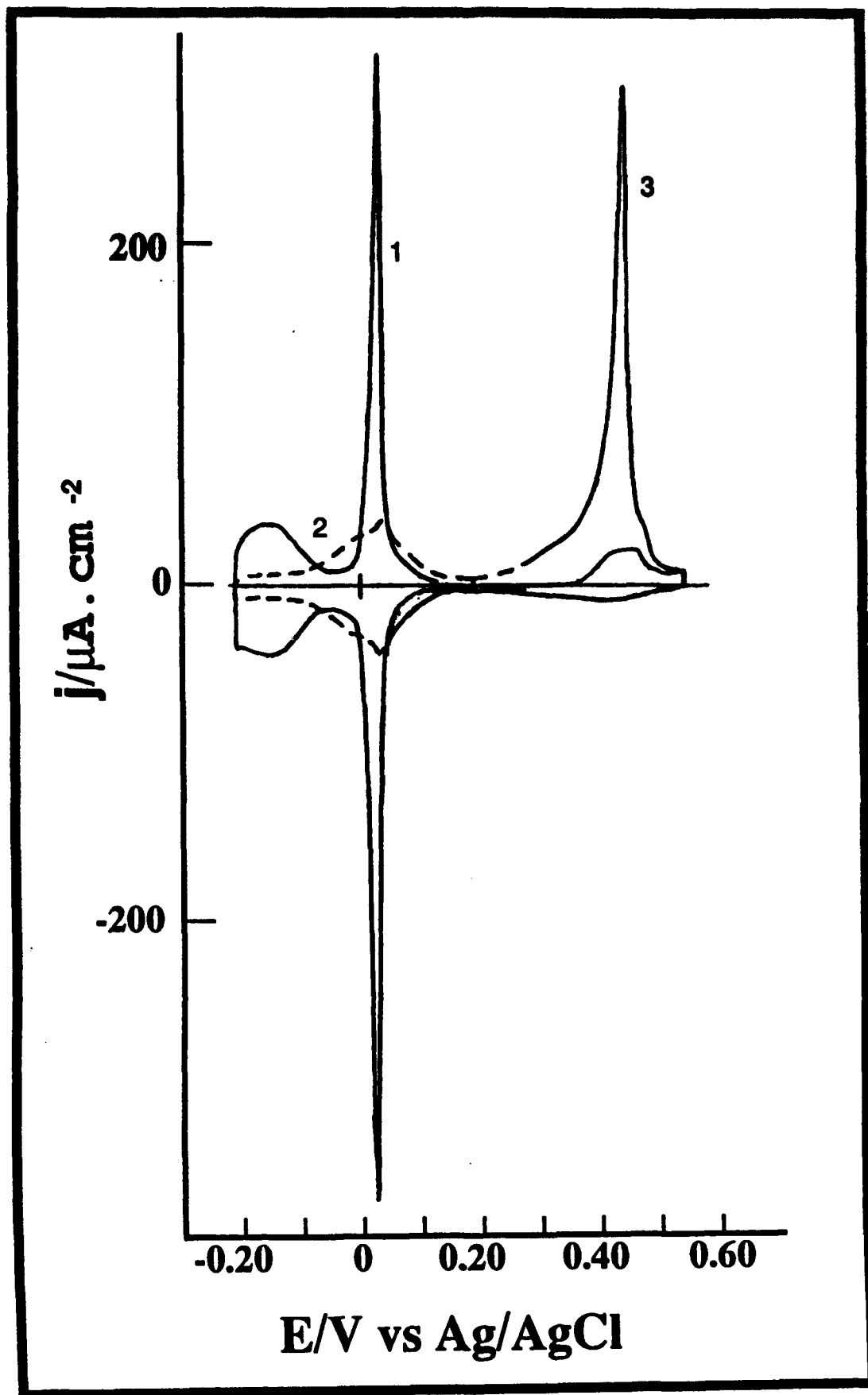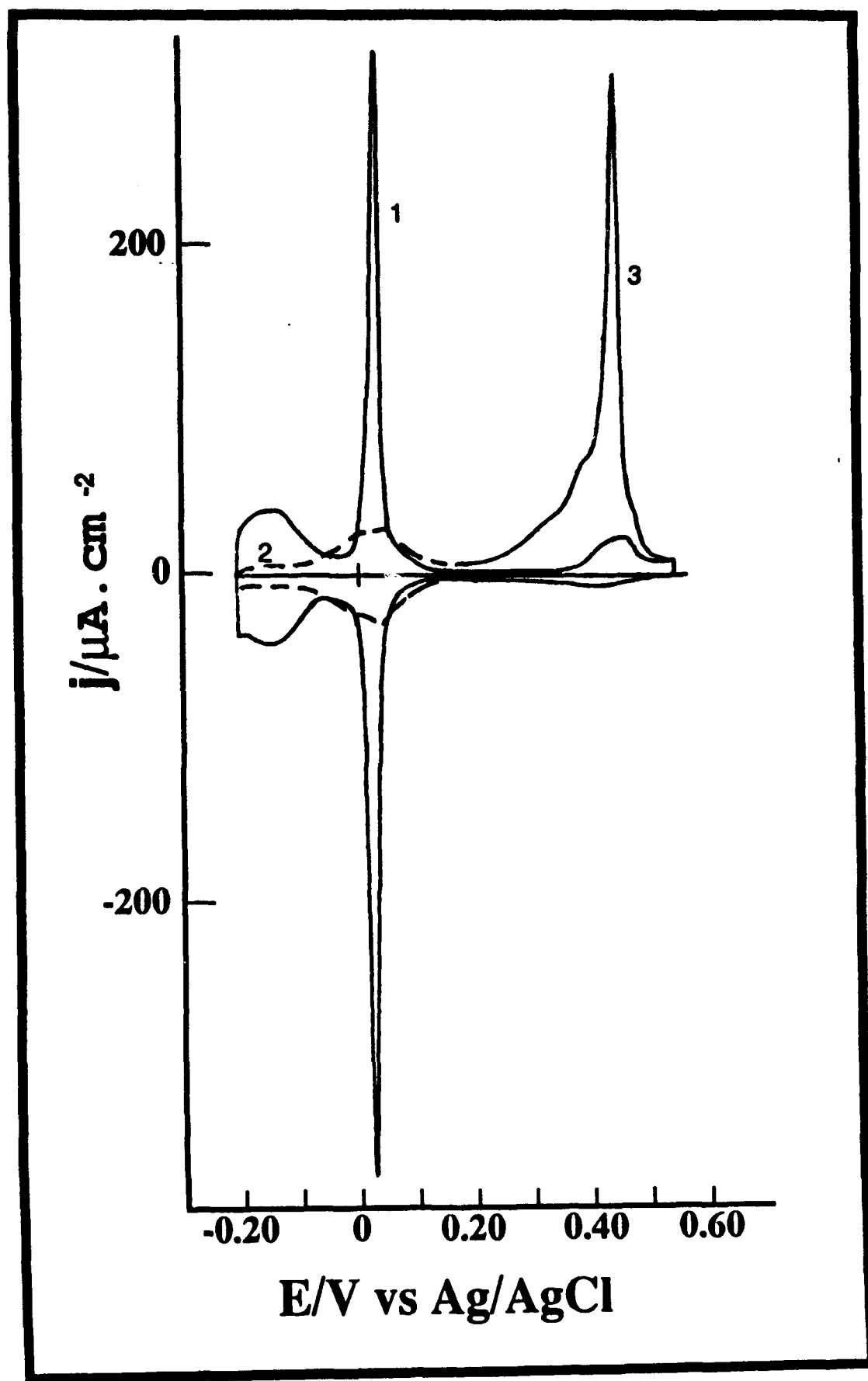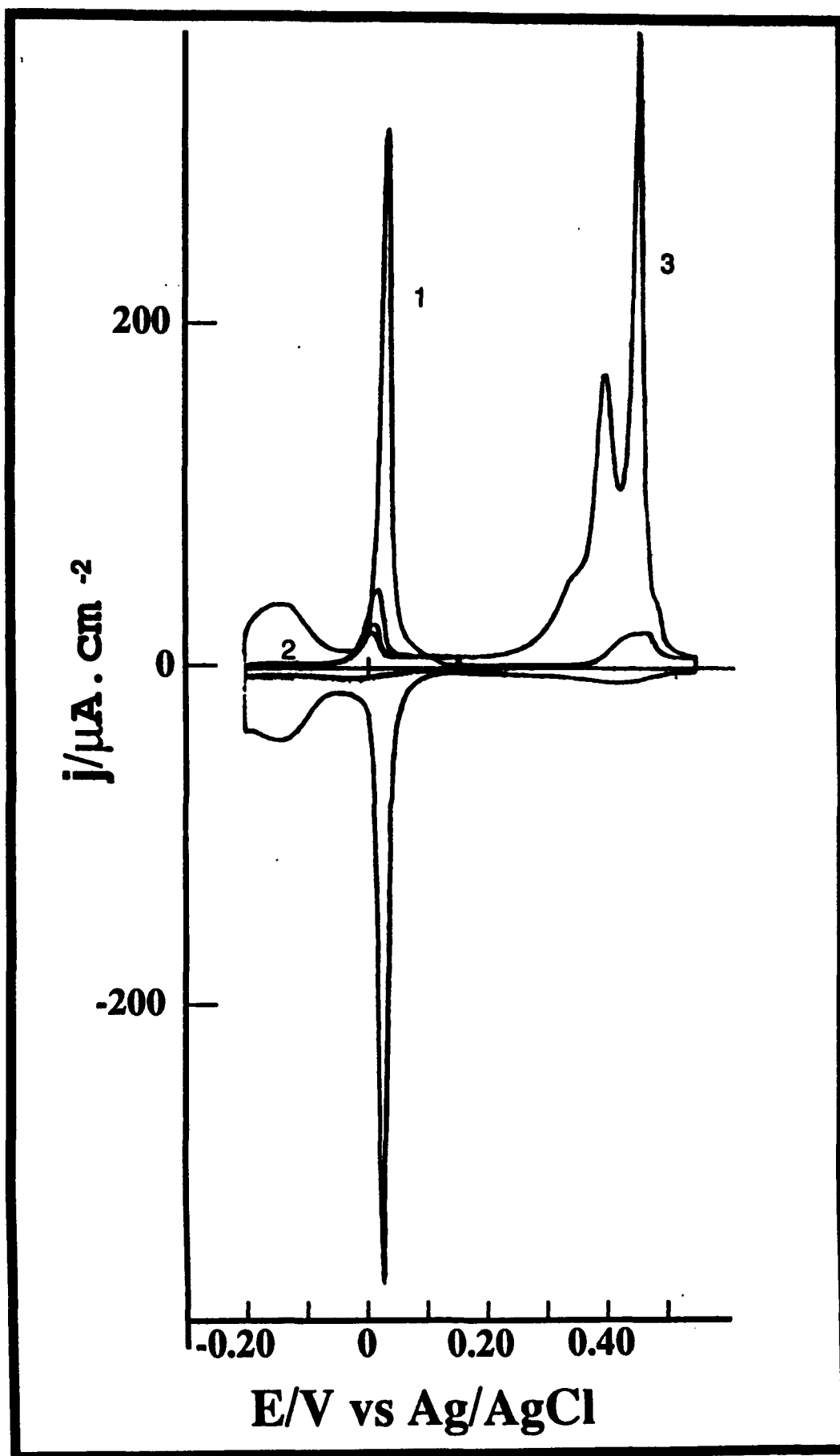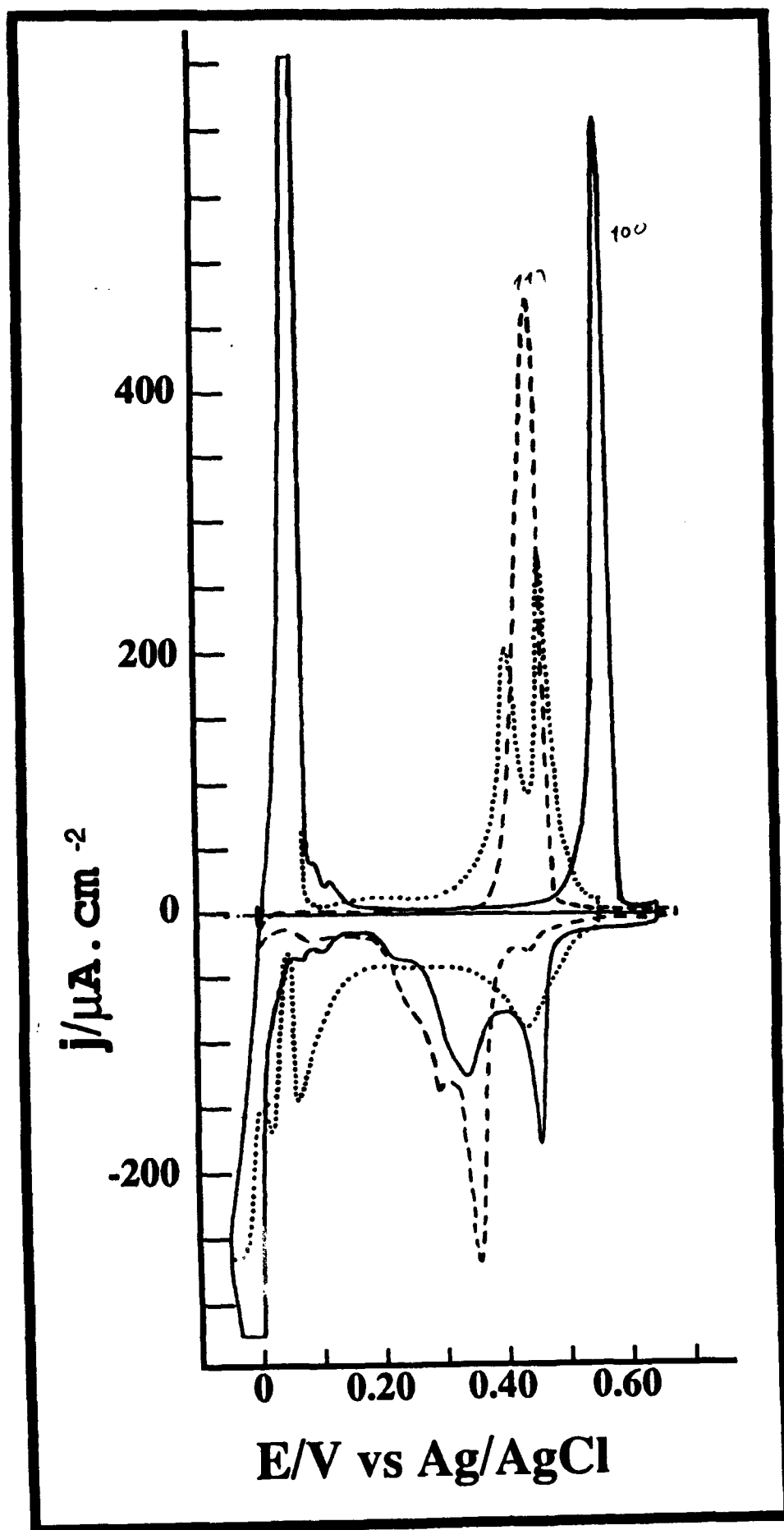
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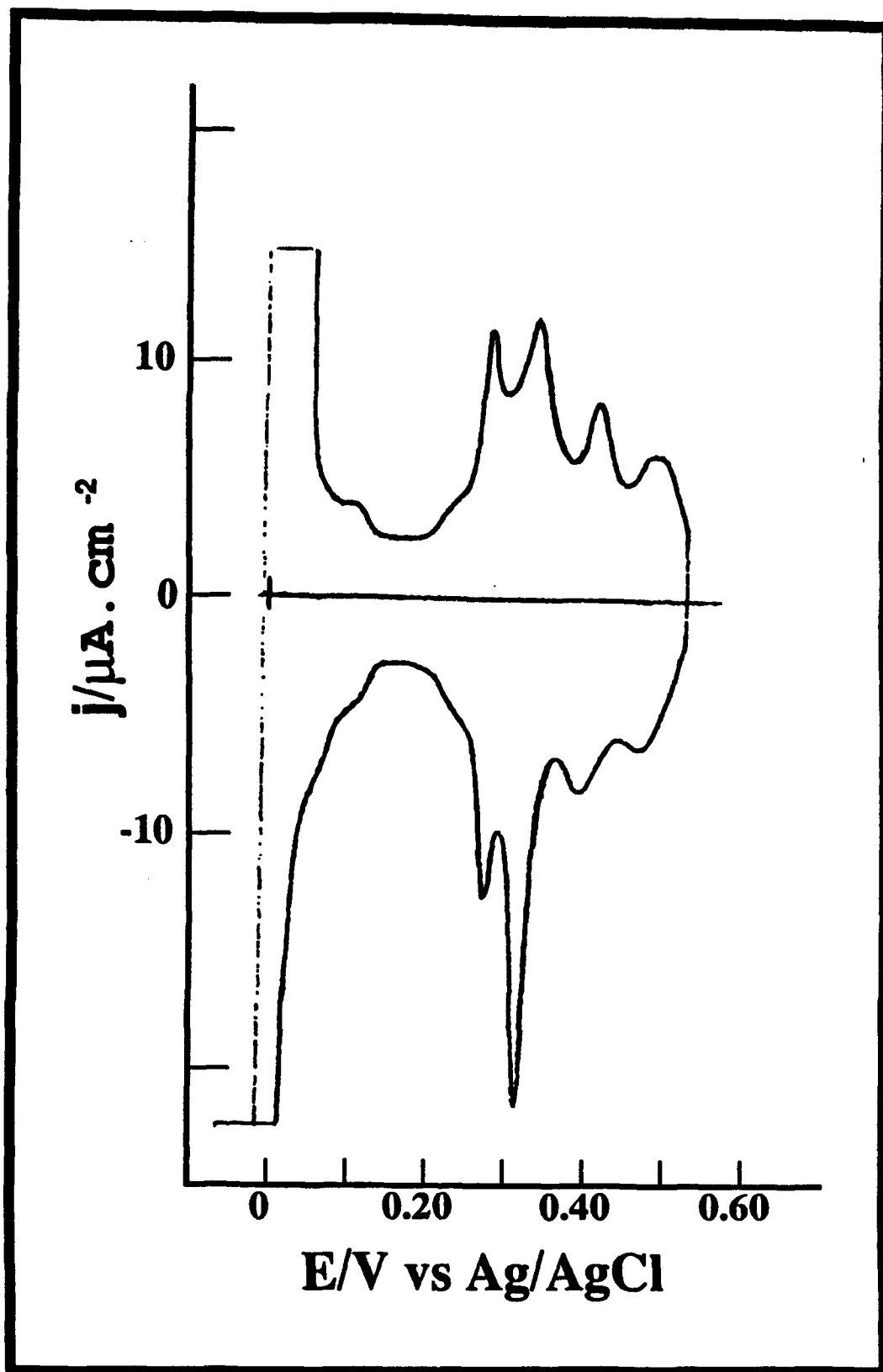
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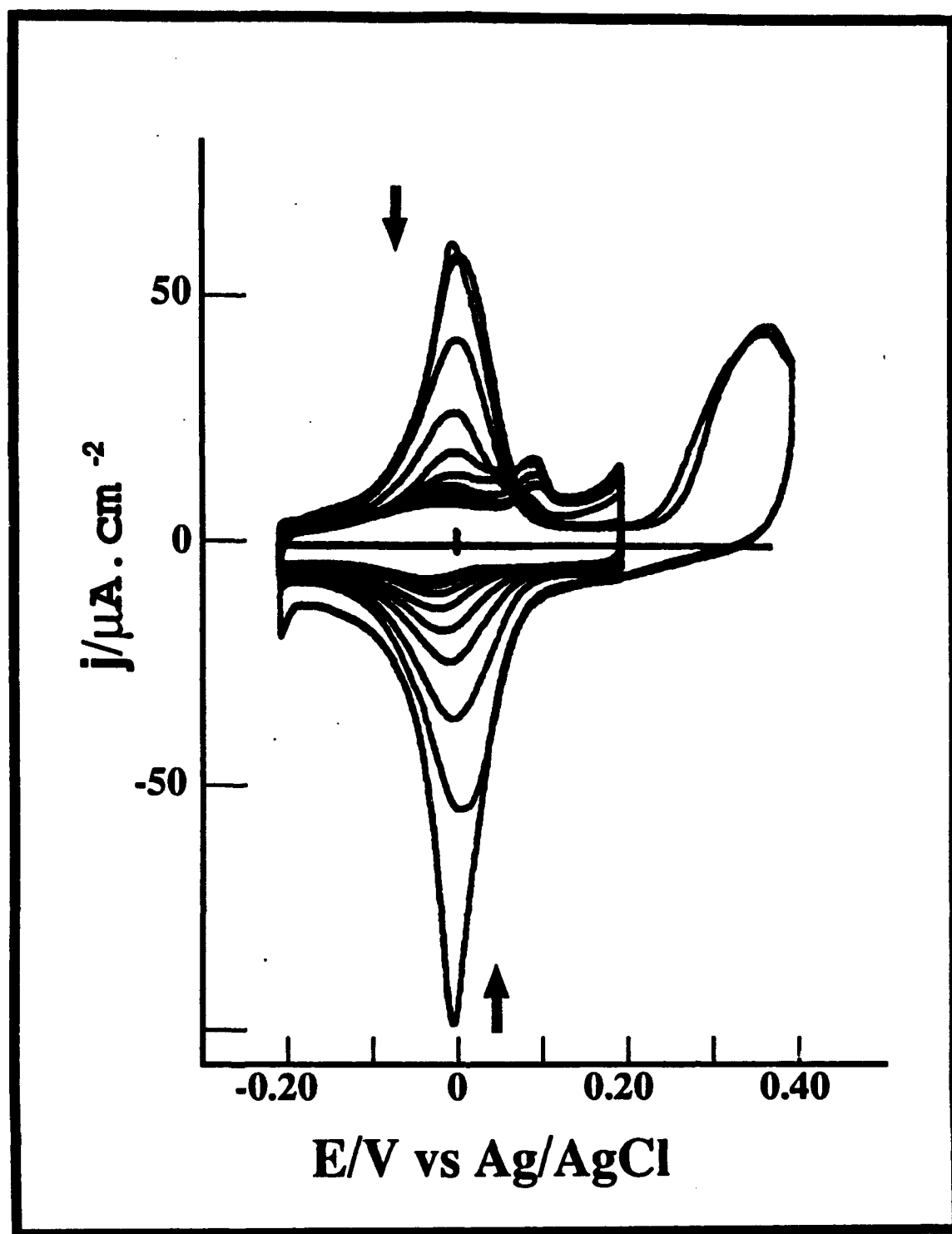
Figure 4

Figure 5

Figure 6a
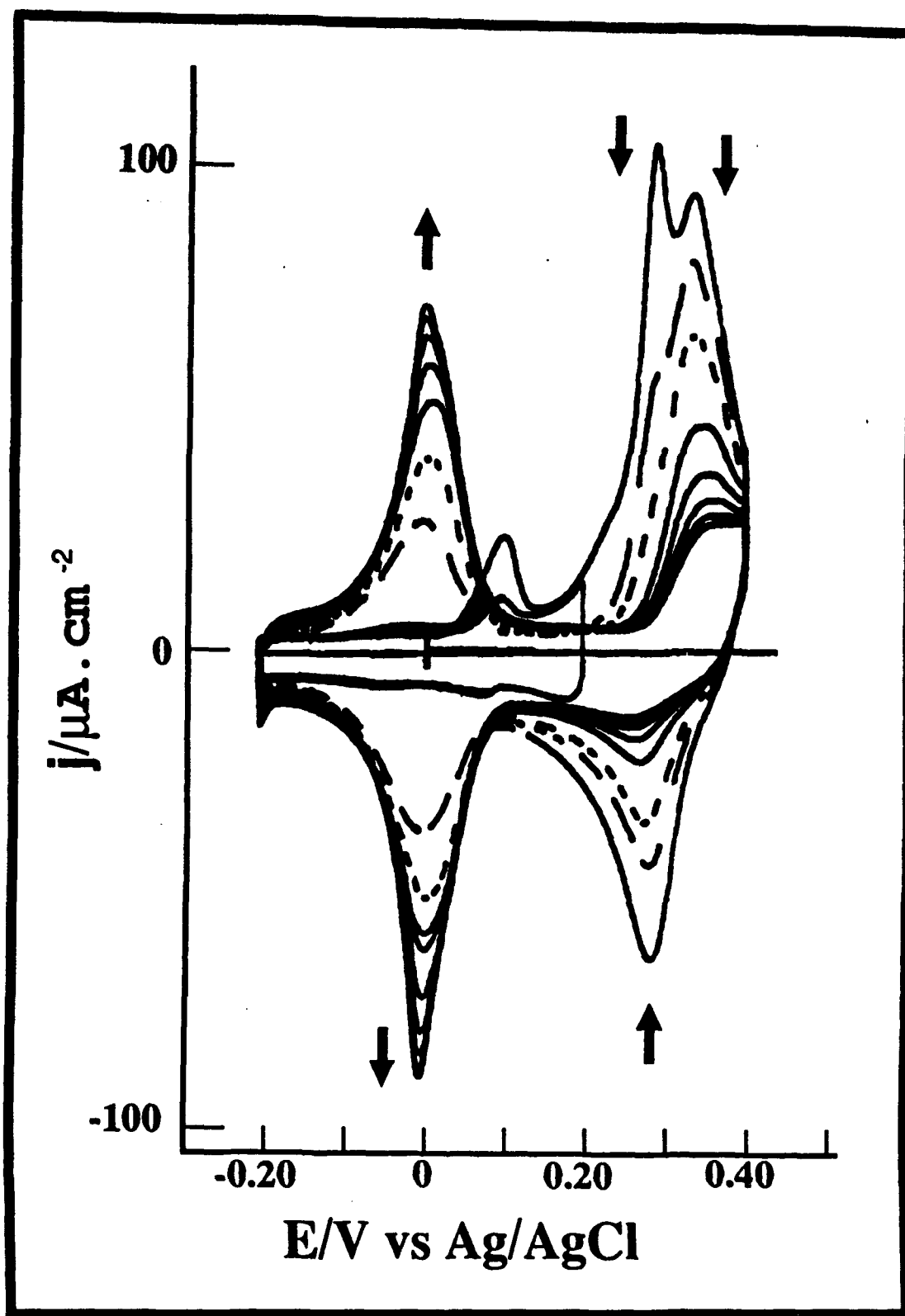
Figure 66

Figure 6C

Figure 7

Figure 8

j/μA . cm⁻² (y-axis label)

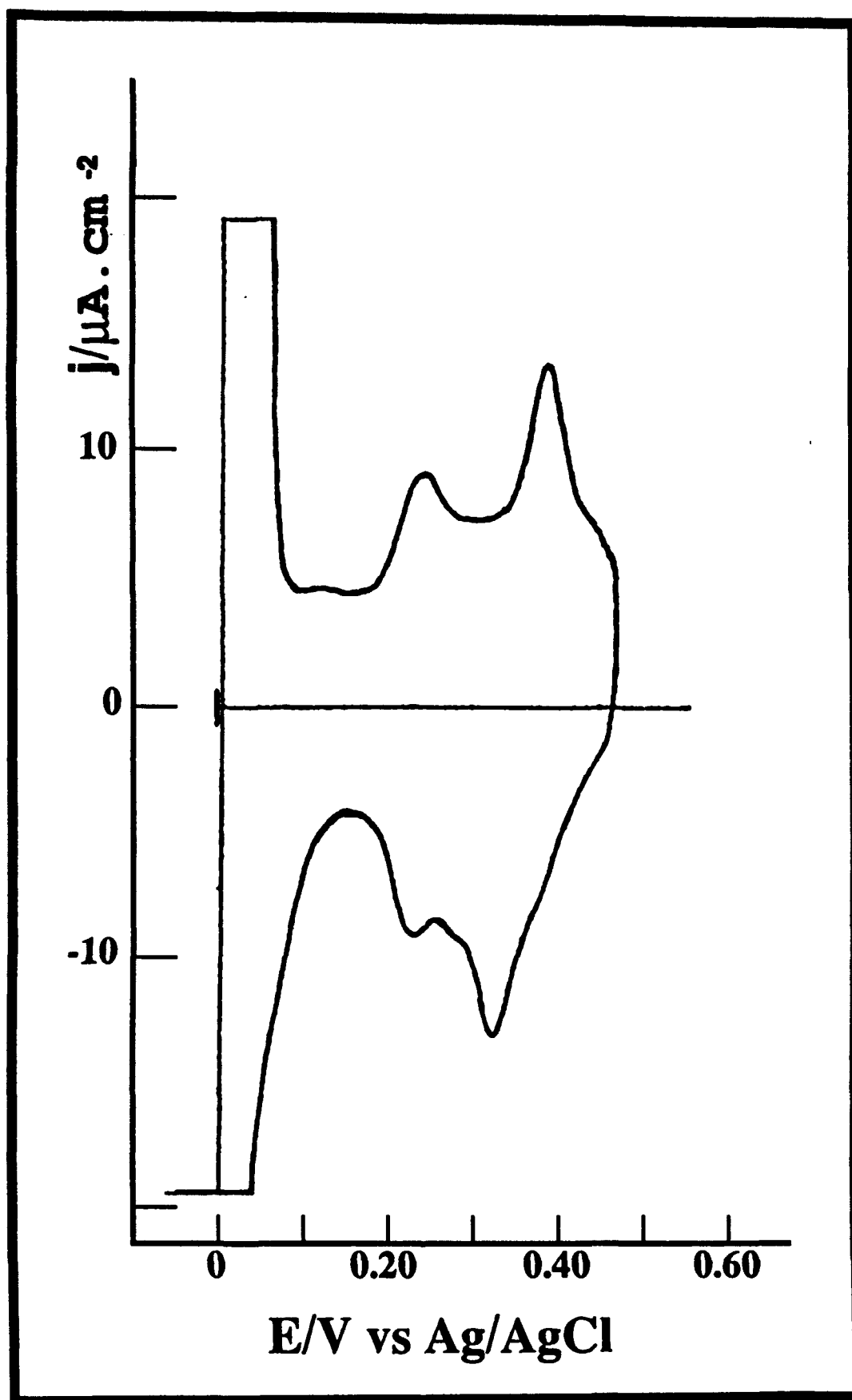y-axis values: 60, 0, -60

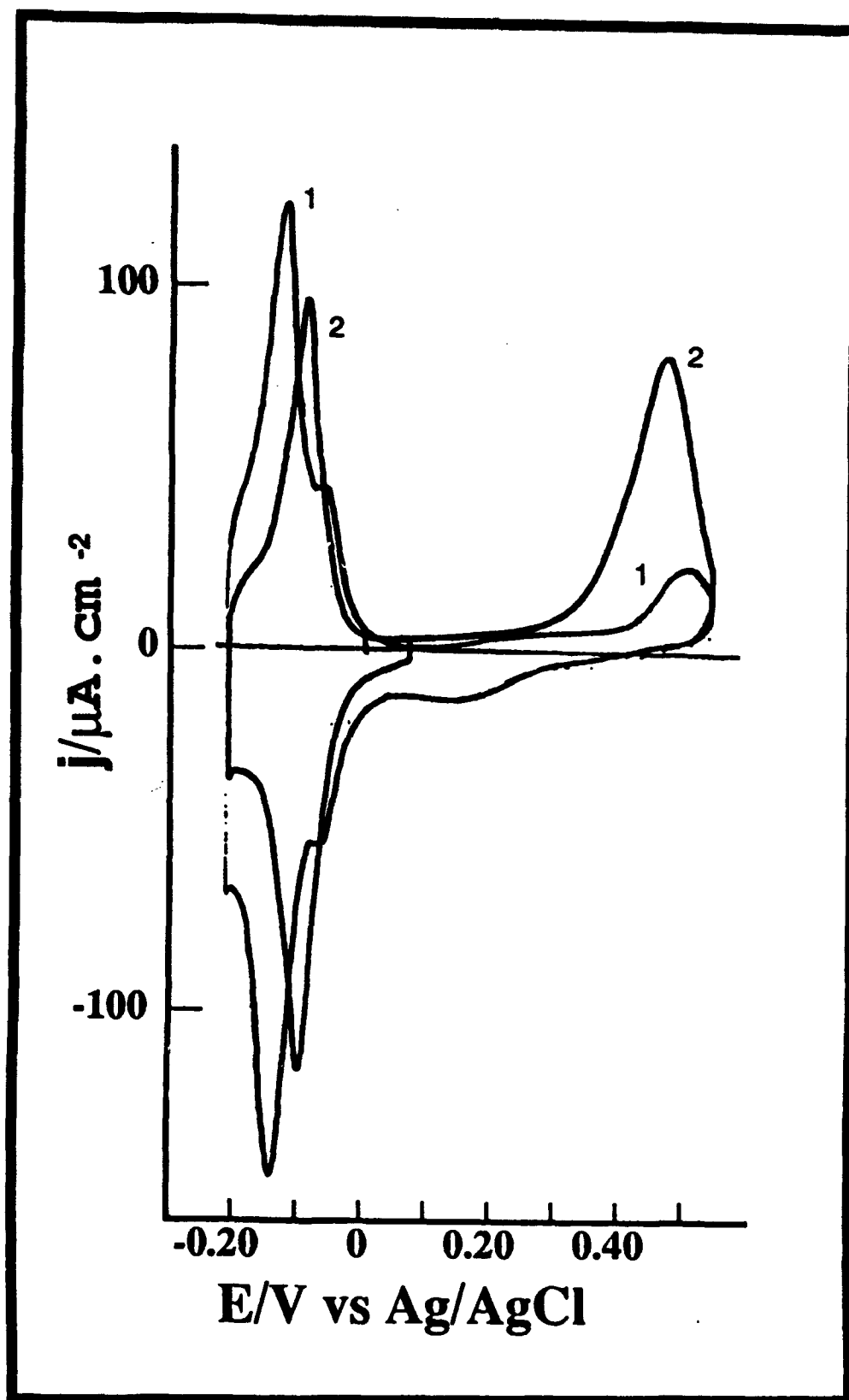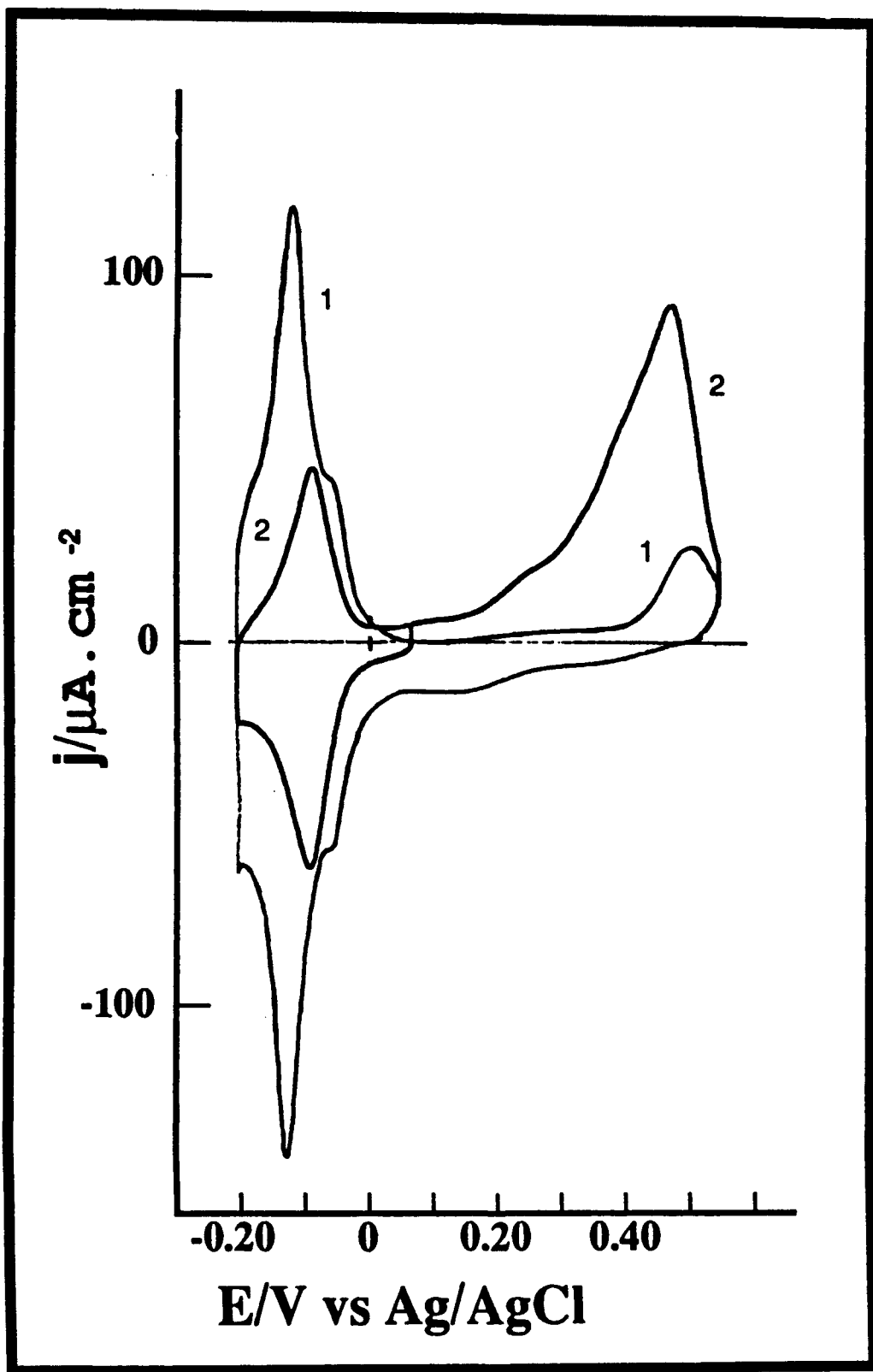**E/V vs Ag/AgCl** (x-axis label)

x-axis values: 0, 0.20, 0.40, 0.60

Figure 9

Figure 10a

Figure 105

Figure 10C

Figure 4